Indian J. Phys. 50, 650-658 (1976)

Analysis of abnormal bond lengths of phenanthrenoid group of compounds specially those containing hetero-atom-N.

PRIYOBROTO ROY CHOWDHURY

Department of Physics, Presidency College, Calcutta 700012

(*Received* 18 *December* 1975)

The characteristic feature of all phenanthrenoid group of compounds is the considerable lengthening of the contact bond linking the two benzenoid rings, and the shortening of the bond opposite to this peri-bond than the normally expected bond distances. The presence of a hetero-atom-N in the phenanthrenoid set of rings is found to be associated with additional bond abnormalities specially the hyper-shortening of a C–N bond and an over-lengthening of an adjacent C–C bond These peculiar bond features were analysed from different angles. Molecular orbital calculations were also made to justify these bond peculiarities.

1. INTRODUCTION

A study of bond lengths of phenanthrenoid group of compounds revealed certain very interesting features specially those containing hetero-atoms. There are marked differences in bond lengths and angles within each ring—the bond lengths frequently varying from the standard values as is clearly seen from Table 3 whtere the ranges of the values of bond lengths and angles in some of these compunds are listed. Here considerable deviation of the C–C bond length from the values of 1.397 ± 001Å found for gaseous benzene by Raman spectroscopy (Langseth & Stoicheff 1956) and electron diffraction (Kimura & Kubo 1960), and that found in crystalline benzene by X-ray diffraction $1.392 \pm .004$Å(Cox *et al*, 1958) is observed. The bond angles also deviated from the theoretical value 120° of the Sp^2 hybridisation. The reasons behind this type of variation which are found to be present in the structures based on conjugated rings analysed frequently uptil now are generally attributed to be arising out of intra-molecular forces, dissimilar environment of the different atomic sites and some other complicated interaction characteristic of the molecular state of the material.

A scrutiny of these phenanthrenoid group of compounds revealed certain common bond features. It was observed that the bond linking the two benzenoid rings was found to be much longer than the normal aromatic C–C distance (1.396Å). The lengthening of the C–C contact bond is in fact, a characteristic feature of aromatic molecules containing a phenanthrenoid arrangement of rings where the carbon framework is less rigid than in the anthracene like arrangement. A typical example is the length of peribond in perylene (Camerman & Trotter, 1964) in which the value is 1.471Å. A value of 1.468Å, has been found in

chrysene (Burns & Iball, 1960) and 1.457Å in phenanthrene (Kay *et al* 1971). In the regular model of each of these molecules (this assumes an ideal planar geometrical molecule with all C–C lengths 1.397Å, and C–H lengths 1.08Å obtained from the spectroscopic estimate of the C–H length in benzene and all angles 120°) the hydrogen atoms in the ortho-positions to the bonds concerned are 0.68Å closer than the sum of their van der Waal radii of 2.4Å. Cruickshank, Sparks and others have attributed this experimentally observed C–C bond lengthening to the effect of steric repulsion between over-crowded hydrogen pair although the crowding is not relieved by C–C bond lengthening. The question now arises whether the hydrogen over-crowding can have an important bearing on C–C bond lengthening. In the case of carbazole compound (Kurahashi *etal* 1969 ; B. N. Lahiri, 1969) it was observed that the contact bond linking the two benzenoid ring was 1.479Å about 0.08Å longer than the normal aromatic C–C distance (1.396Å) even though this molecule is free from steric hindrances —the non-bonded intra-molecular separation between the pair of hydrogen concerned in the regular model is 0.2Å greater than the normal van der Waal's separation of 2.4Å. It therefore serves as an example of C–C lengthening in a phenanthrenoid arrangement of benzenoid rings free from hydrogen over-crowding and positively suggests that the preconception of aromatic C–C lengthening due to steric hindrance is of doubtful validity. Additional support for this conclusion comes from the results of theoretical calculations of Coulson & Skancke (1962). These authors have calculated the effect of steric repulsions between hydrogen atoms in the ortho position to the peribond connecting the two naphthalene unit of perylene. Their results show that the repulsive interaction between the ortho-hydrogens cannot be responsible for the experimentally observed increase in the peri-bond.

This lengthening of the contact bond' linking the two benzenoid rings may be analysed from a different angle. The three fused rings of the phenanthrenoid set up may be considered to have a biphenyl part (ring 1 & 3) to which a group of atoms is attached to form the central ring. The peribond in the phenanthrenoid class of compounds was found to be invariably smaller than the value for the equivalent bond found in the structures of biphenyl (Hargreaves & Rizvi 1963)—a value of 1.507Å was obtained by Trotter which is only slightly short of the usually accepted Sp^2—Sp^2 single bond value of 1.517Å. It is perhaps likely that the linkage of this atomic group with the biphenyl rings results in an extended electron system within the molecule and the contact bond which now forms an arm of the six mebered central ring (2) acquires a strong tendency to move towards the value for a partial double bond although it cannot approach it. It may be suggested that the π-electron delocalisation responsible for attributing double bond character in a conjugated system is significantly stronger in the above case than what is found in the case of biphenyl.

Another typical characteristic feature of aromatic molecules containing a phenanthrenoid arrangement of rings is that the bond opposite to the lengthened contact bond is invariably shorter than the normally expected bond distances. The predominance of the single bond character of the contact bond and the predominant double bond character of the bond opposite to it can be explained to a limited extent assuming that a stable configuration is achieved only when such a situation prevails. This is quite evident from figures 1(a, b, c, d, e)—the

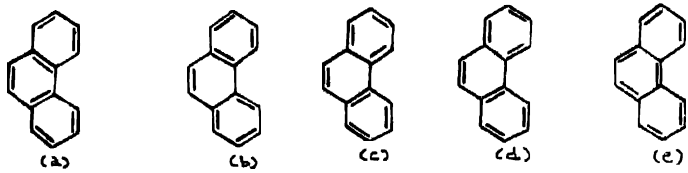

Fig. 1. The canonical structures of phenanthrenoid arrengement of rings.

canonical structures represented in figure 1(a) contributes mostly to the resonance hybrid since it represent a stable benzenoid configuration. In fact bond lengths in structures based on conjugated rings which deviate considerably from the standard values are to an extent influenced by the predominance of the double or single bond characteristic necessary for the structure to make the maximum contribution to the resonance hybrid. However such an analysis may be considered to be very gross and does not take into account the complicated interactions of the molecular state such as intramolecular forces which may distort the molecule from its ideal planar state.

As a part of the general programme of study on those phenanthrenoid group of compounds containing hetero-atom as regards their structural deviations from the parent compound, molecular structure of phenanthridine (Roy Chowdhury 1973) was experimentally determined and attempts to analyse the abnormalities in bond lengths specially those arising due to the introduction of the hetero-atom was carried out. In the ring makred II which is essentially a pyridine configuration the remarkable feature is the hypor shortening of C(13)–N(14) bond (1.291Å) and the considerable lengthening of the C(12)–C(13) bond (1.487Å) as well as the relative shortening of the C(1)-N(14) bond compared to the corresponding bonds of phenanthrene $C_{14}H_{10}$. Here also the extended peribond C(6)–C(7) was also observed. Though the general trends of these bond lengths of phenanthridine together with similar trends observed in the corresponding bonds of phenanthrene, chrysine, phenanthridone (Sen 1970) etc. can to a limited extent be explained from the assumption that such trends in the bond length are compatible with the canonical structure which contributes mostly to the resonance hybrid and represents a stable benzenoid configuration, yet the remarkable feature observed in the case of phenanthridine is that the deviation in bond lengths of C(13)-C(12)

and C(13)–N(14) appeared exaggerated and C(1)–N(14) bond more controlled than the purely benzenoid hydrocarbon counterpart phenanthrene. This difference may therefore be attributed to the presence of the hetero-atom nitrogen.

The stable configuration of phenanthridine demands the lengthening of C(1)—N(14) bond on account of the predominance of single bond character—a feature observed in the corresponding bond distance in phenanthrene. But contrary to this no elongtion of C(1)–N(14) bond distance (1.391Å) was observed. This is probably due to the effect of pyridine ntrogen which has a higher electronegativity. The relatively shortened C–N bond distance when a nitrogen replaced carbon in the six membered ring is characteristic of many aromatic compounds. The shortened C–N bond distance of 1.339Å in pyridine (Bak *et al* 1958) corresponds to a C–C bond of 1.39Å in benzene. The shortening of the related bond when a pyridine type nitrogen is present in a six membered ring is also observed in pyrimidine (Whoatley 1960). From this it may reasonably be assumed that in the case of C(1)–N(14) bond in phenanthridine the shortening effect of the pyridine-type nitrogen will be counteracting the lenghening tendency arising out of the predominance of the single bond characteristic for a stable configuration. Again the hyper-shortening of C(13)–N(14) bond in phenanthridine may be interpreted as due to the shortening effect of the electronegative pyridine type nitrogen together with the added shortening tendency due to the predominance of double bond characteristic of this bond. The overlengthening of C(12) –C(13) bond (1.486Å) may be attributed partially to the predominance of the single bond character of that bond (figure 2) and also to the tendency of the

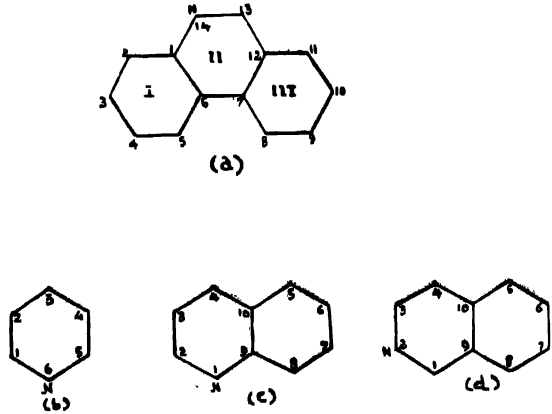

Fig. 2. Conventional structural formulae for the compounds investigated in π-electron calculation (a) phenonthridine (b) pyridine (c) quinoline (d) isoquinoline.

C(13) atom to move towards the nitrogen thereby causing the additional lengthening of C(13)–C(12) bond at the cost of shortening the C(13)–N(14) bond.

With the progress of MO theories during the last decade it is now generally expected that the in-plane deformation found in the molecular geometry can be accounted for, on the basis of π-electron delocalisation of different degree at different atomic cores due to interactions between atoms forming dissimilar environment at each atomic site. In order to justify the irregularities and deviations of bond lengths of conjugated hetero-aromatic molecules specially those containing the pyridine-type nitrogen the bond characteristics of phenanthridine, quinoline, isoquinoline and pyridine were investigated by molecular orbital calculations of bond lengths via bond orders from a self consistent field approach using π-electron orbitals on all atoms in the molecular ring. Calculations in the Huckel approximation (Huckel 1931) and in the LCAO-SCF approximation (Roothaan 1951) using the semi-emperical Pariser-Parr-Pople method (Pariser & Pople 1953) were carried out for these four hetero-aromatic compounds. The Huckel calculations were performed in the usual way where the exchange parameter (kcx) and Coulomb parameter (h_x) corresponding to the hetero-atomnitrogen(N) were chosen to be unity. The coefficients of the atomic orbitals, obtained by the Huckel procedure, were used as the starting coefficients for the SCF calculations i.e. to evaluate the mobile bond orders p_{rs} and the matrix elements of the one-electron Hatree-Fock-Hamiltonian operator F_{rs} and hence to solve the secular equations for the energies of the individual molecular orbitals, and then a set of coefficients were determined by direct solution of Hatree-Fock-Roothan equations (Roothaan 1951). Iterative process was adopted to calculate the one electron self consistent M.O. The numerical solution of the SCF equations for the molecular ground states, based on single determinant wave function was evaluated on CDC 3600 computer at T.I.F.R. Bombay. Self consistency was taken to a precision of 10^{-4} for fond orders. Two alternative approximations referred to as the Mataga-Nishimoto (MN) (Mataga & Nishimoto 1957) and Beveridge—Hinze (BH) (Beveridge & Hinze 1971) evaluations were used for calculating the two centre Coulomb repulsion γ_{rs} as a function of the inter-nuclear distance R_{rs} (obtained from the geometrical dimension of the molecule). Further two independent methods denoted as Pariser & Parr (PP) (Parr 1964) and Nishimoto-Forester (NF) (Nishimoto & Forester 1965) evaluations were used for calculating the nearest neighbour core resonance integral β_{rs}. The non-neighbour core resonance integral β's could be neglected without introducing any error of greater magnitude than those introduced by other assumptions such as zero differential overlap.

Four different selections of $\gamma-\beta$ values are then possible in accordance with the scheme given below :

(1) Mataga-Nishimoto γ, Pariser-Parr β
(2) Beveridge-Hinze γ Pariser-Parr β

(3) Mataga-Nishimoto γ, Nishimoto-Forester β
(4) Beveridge-Hinze γ, Nishimoto-Forester β

For the calculation of γ and β the molecular geometries are necessary. The molecules under consideration were assumed to be planar and each six membered ring was assumed to be a regular hexagon with all bond lengths equal to 1.4Å. A set of coordinates obtained from the regular geometry of each molecule was used to calculate inter-nuclear distances R_{rs} within it.

Four separate computations were run on the molecule phenanthridine with the object of testing the relative merits of different choices of approximations for the evaluation of integrals γ and β and to gauge the extent of dependence of bond length on them. The values of the valence-state ionisation potentials and one-centre Coulomb repulsion integrals used in these calculations were taken from the work of Beveridge & Hinze (table 1). From a close scrutiny of the calculated bond lengths it was observed that the bond lengths are rather insensitive to the different choice of approximations used for evaluating the integral γ but are significantly sensitive to the choice of β. Table 2 lists the results using the relatively better pairs —Set (1) and Set (4), together with the experimental geometry of the phenanthridine molecule as obtained by the author by X-ray method. Two independent set of SCF calculations were carried out on all the three compounds (pyridine, quinoline, and isoquinoline) containing pyridine nitrogen using the two relatively better suited pairs; set (1) PPβ, MNγ and set (4) NFβ, BHγ. The results of these calculations are also listed in Table (2). The conventional structural formulae and numbering of atoms in the molecule are shown in figure 2. In the case of these three compounds experimental data on bond lengths are yet to be reported except in the case of pyridine whose geometry has been determined from micro-wave spectra by Bak *et al.*

The values of the SCF parameters and relevant quantities used in the present calculation are listed in table 1

Table 1a. Values of the valence-state ionisation potentials and one-centre Coulomb repulsion integrals for various atoms, taken from the work of Beveridge & Hinze. Assumed values of the empirical constants B for PP evaluation of β, taken from the paper by Kupriech, Danilov & Shramko

Atom	Valence-state electron configuration	Valence-state ionisation pot. (ev)	One-electron repulsion integral (ev)	Empirical constant B (ev)
C^+	tr tr tr π	11.16	11.13	2518
N^+	tr tr tr π	14.12	12.34	2335

Table 1b. Values of empirical constants A_0 and A_ε for NF evaluation of β and those of emperical constants L_0 and L_1 in order:length relation for CC, CN taken from the paper by Nishimoto and Forester

Bond	$n=1$	A_{02} (ev)	3	A_ε (ev)	L_0(Å)	L_1(Å)
CC	−2.04	−1.90	−1.84	−0.51	1.517	0.18
CN	−2.24	−2.09	−2.02	−0.53	1.451	0.18

$-n$ being the number of rings in the molecule

The results of the present calculations of phenanthridine do not seem to agree ideally with the experimental data Some of these predicted bond lengths are smaller and some larger than those observed experimentally. However, this type of disagreement between the experimental and theoretical results is not uncommon and an example of similar compound phenanthrene may well be cited. Here the experimental bond lengths as reported by Kay *et al* do not match very well with those predicted theoretically by Skancke (1965). Inspite of these disagreements, theoretically calculated values of bond lengths successfully represent the general features of the molecular geometry. The primordial concern of the present study is to understand the structural deviations specially those arising due to presence of hetero-atom nitrogen. The hyper-shortening of the C(13)-N(14) bond and the over-lengthening of the adjacent C(12)-C(13) bond can to a great extent be accounted from the present theoretical calculations. C(12)-C(13) bond distance was calculated to be the largest and the C(13)-N(14) bond calculated to be the shortest, the values agreeing very satisfactorily with the experimental result. Moreover the lengthening of C(6)-C(7) peribond is clearly represented in the relatively large calculated value of C(6)-C(7) bond distance Since the effects of the hydrogen atoms have been left out of the calculations completely by the relative lengthening of the C(6)-C(7) peribond predicted theoretically seem to imply that the main cause of lengthening of this bond lies in the π-electron delocalisation and confirms the doubtful validity of the theory that the C–C bond lengthening is a result of the steric repulsion between over-crowded hydrogen pair

On scrutinizing carefully the results of theoretical study listed in table 2 it is observed the series pyridino-quinoline-isoquinoline also exhibited a hyper-shortening of a C–N bond and an over-lengthening of an adjacent C–C bond similar to that observed in phenanthridine. In both quinoline and isoquinoline the bond corresponding to the peribond in phenanthridine showed a lengthening tendency. These bond distances are seen to be also to some extent influenced by the σ-skeleton (nuclear skeleton). A study of the pyridine-quinoline-isoquinoline-phenanthridine series revealed that the bond lengths corresponding to C(12)–C(13) and C(6)–C(7) bonds of phenanthridine increases while those corresponding to C(13)–N(14) bond of phenanthridine decreases with the increase in the number

of benzenoid rings. The results suggest that the π-electrons in the pyridinoid ring of the two ringed and three ringed system are partially delocalised.

Table 2. Theoretical bond lengths together with those obtained experimentally.

Compound	Bond	Experimental length (Å)	Theoretical bond length (Å) Set 1	Set 4
Pyridine	C(2)–C(1)	1.3958	1.400	1.398
	C(3)–C(2)	1.3936	1.395	1.397
	N(6)–C(1)	1.3394	1.332	1.334
Quinoline	C(2)–N(1)		1.301	1.319
	C(3)–C(2)		1.431	1.414
	C(4)–C(3)		1.363	1.381
	C(6)–C(5)		1.361	1.380
	C(7)–C(6)		1.433	1.415
	C(8)–C(7)		1.361	1.371
	C(9)–C(8)		1.436	1.423
	C(9)–N(1)		1.371	1.356
	C(10)–C(4)		1.430	1.421
	C(10)–C(5)		1.434	1.422
	C(10)–C(9)		1.389	1.417
Isoquinoline	N(2)–C(1)		1.302	1.319
	C(3)–N(2)		1.369	1.349
	C(4)–C(3)		1.368	1.382
	C(6)–C(5)		1.361	1.381
	C(7)–C(6)		1.433	1.415
	C(8)–C(7)		1.361	1.381
	C(9)–C(1)		1.431	1.422
	C(9)–C(8)		1.434	1.422
	C(10)–C(4)		1.427	1.421
	C(10)–C(5)		1.435	1.422
	C(10)–C(9)		1.387	1.417
Phenanthridine	C(1)–C(2)	1.392	1.430	1.416
	C(1)–C(6)	1.419	1.386	1.411
	C(1)–N(14)	1.391	1.381	1.372
	C(2)–C(3)	1.409	1.364	1.386
	C(3)–C(4)	1.420	1.428	1.408
	C(4)–C(5)	1.387	1.365	1.387
	C(5)–C(6)	1.424	1.429	1.414
	C(6)–C(7)	1.475	1.450	1.448
	C(7)–C(8)	1.417	1.429	1.414
	C(7)–C(12)	1.426	1.384	1.410
	C(8)–C(9)	1.352	1.365	1.387
	C(9)–C(10)	1.437	1.427	1.408
	C(10)–C(11)	1.417	1.365	1.386
	C(11)–C(12)	1.410	1.428	1.415
	C(12)–C(13)	1.486	1.455	1.450
	C(13)–N(14)	1.291	1.205	1.307

Table 3 Comparative study of ranges of bond lengths and angles observed in some of the structures analysed uptil now, with that observed in the present study

	Phenanthrene	Perylene	Chrysene	Phenanthridone	Cyclopentano phenanthrene	Present study of phenanthridine
Bond length (Å)	1.357–1.445	1.363–1.439	1.361–1.427	1.357–1.431	1.343–1.449	1.352–1.437
Bond angles	118.1°-123.2°	118.0°-121.7°	118.4°-122.9°	116.6°-124.4°	116.2°-124.4°	115.8°-125.8°

References

Bak B., Hansen-Nygaard L. & Rastrup Andersen J. 1958 *J. Mol. Spectry.* **2**, 361.

Beveridge D. L. & Hinze J. 1971 *J. Amer. Chem. Soc.* **93**, 3107

Burns D. M. & Iball J. 1960 *Proc. Roy. Soc.* **A 257**, 491.

Camerman A. & Trotter J. 1964 *Proc. Roy. Soc.* **A 279**, 129.

Cox E. G., Cruickshank D. W. J. & Smith J. A. S. 1958 *Proc. Roy. Soc.* **A247**, 1

Coulson C. A. & Shanckc P. N. 1962 *J. Chem. Soc.* 2775

Cruickshank D. W. J. & Sparks R. A. 1960 *Proc. Roy. Soc.* **A258**, 270.

Hargreaves A. & Rizvi S. H. 1962 *Acta Cryst.* **15** 365.

Huckel E. 1931 *Z. Physik.*, **70**, 204.

Kay M. I., Okaya Y. & Cox O. E. 1971 *Acta Cryst.* **B27**, 26

Kimura K. & Kubo M. 1960 *J. Chem. Phys.* **32**, 1776.

Kuprevich V. A., Danilov V. I. & Sharanko O. V. 1966 *Theo. & Expt. Chem.* **2**, 535.

Kurahashi M., Fukuyo M., Shimada A., Furusaki A. & Nitta I. 1969 *Bull. Chem. Soc. Japan* **42**, 2170.

Langseth A. & Stoichoff B. P. 1956 *Can. J. Phys.* **34**, 350.

Lahiri B. N. 1969 *Acta Cryst.* A255 127, XIII-4

Mataga M. & Nishimoto K. 1957 *Z. Physik. Chem.* (Frankfurt) **13**, 140

Nishimoto K. & Forester L. S. 1965 *Theo. Chim. Acta*, **8**, 407.

Pariser R. & Parr R. G. 1953 *J. Chem. Phys.* **21**, 466.

Pople J. A. 1953 *Trans. Farad. Soc.* **49**, 1375.

Parr R. G. 1964 *The Quantum Theory of Molecular Electronic Structure*, Benjamin Inc. 503.

Roothaan C. C. J. 1951 *Revs. Mod. Phys.* **23**, 69.

Roychowdhury P. 1973 *Acta Cryst.* **B29**, 1362

Sen D. K. 1970 *Acta Cryst.* **B26**, 1629.

Skancke P. N. 1965 *Acta Chem. Scand.* **19**, 401.

Wheatley P. J. 1960 *Acta Cryst.* **13**, 80.